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GROWTH AND LUMINESCENCE SPECTROSCOPY OF
A CuCl QUANTUM WELL STRUCTURE

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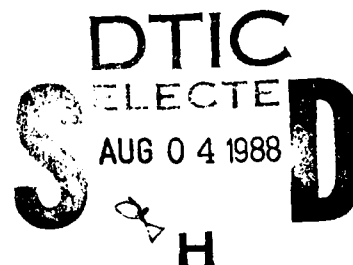
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Abstract

A structure of the type $\text{CaF}_2/\text{CuCl}/\text{CaF}_2$, in which the confined layer is 150 Å thick, has been grown on a Si(111) surface by molecular beam epitaxy in ultra-high vacuum. The optical properties of the CuCl film have been characterized by low-temperature photoluminescence as a function of excitation density. Striking differences in the excitonic emissions are observed between the quantum well structure and a bulk single crystal of CuCl, and are discussed in terms of film purity and thickness.

I. Introduction

The optical properties of CuCl have been studied for nearly thirty years,^{1,2} and have provided a wealth of information about excitons. In fact, CuCl appears to be an ideal material in which to study

exciton spectroscopy and dynamics, since the free exciton has quite a large binding energy (190 meV) and excitonic molecules (or biexcitons) are formed.³ More recently, there has been a great deal of interest in dimensionally constrained excitons, such as those observed in quantum wells and superlattices.⁴ However, the exciton binding energy in GaAs, which is the basic building block of most of the quantum well systems studied to date, is quite small (4.2 meV). Thus, the excitonic spectra can be difficult to resolve against the band edge in these systems. Also, excitonic molecules are not observed in GaAs. For these reasons, the study of CuCl quantum wells is appealing, since it should be possible to observe and resolve the effects of two-dimensional confinement on the dynamics of both excitons and biexcitons.

Two research groups have reported studies of the effects of quantum confinement on excitons in small CuCl particles. Itoh and Kirihara⁵ have studied NaCl heavily doped with Cu⁺, which contains a large range of particle sizes, by examining emission spectra excited by a tunable dye laser. They observe a set of peaks that shift with excitation photon energy, which they ascribe to quantized states of the excitons in CuCl particles of different sizes. Ekimov, et al.⁶ have grown size-selected CuCl crystallites in an insulating matrix of silicate glass. They observe a definite blue shift of the excitonic absorption spectra with a decrease in CuCl crystallite size. They also observed that the intensity of the bound exciton photoluminescence decreased dramatically with respect to the free exciton as the crystallites got smaller. Payne, et al.⁷ have also observed CuCl emission from microcrystals of CuCl in Cu⁺-doped single crystals of

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SrCl_2 and CdCl_2 , but have not specifically addressed the topic of quantum confinement.

None of the above groups has observed excitonic molecules in the spectra of their materials. We report here the initial observation of photoluminescence from both excitons and biexcitons from a 150Å-thick film of CuCl sandwiched between two CaF_2 layers, as represented schematically in Fig.1.

II. Experimental Procedure

The samples were grown in an ultra-high-vacuum (UHV) chamber (base pressure: 2×10^{-10} torr) equipped with a sample manipulator capable of heating a $\text{Si}(111)$ wafer resistively, two Knudsen cells, and a film-thickness monitor. The $\text{Si}(111)$ substrates were flashed to 1100°C in UHV in a manner shown in previous experiments to produce a surface with a sharp $\text{Si}(111)$ 7×7 Low-Energy Electron Diffraction (LEED) pattern and with no impurities detectable by Auger electron spectroscopy. A 150Å-thick film of CaF_2 was deposited by evaporation of the compound from a single Knudsen cell onto the Si substrate, which was held at a temperature of 700°C.⁸ The pressure in the chamber during this stage was 2×10^{-7} torr. The substrate was then cooled to ambient temperature, and a 150Å-thick film of CuCl was grown on top of the CaF_2 by evaporation from a single Knudsen cell, with the background pressure holding at 2×10^{-8} torr or below. The CuCl film was then capped with a second 150Å CaF_2 film, this time deposited onto the sample at ambient temperature. The total film thickness ($\text{CaF}_2 +$

$\text{CuCl}+\text{CaF}_2$) was measured to be $500\pm 50\text{\AA}$ by scanning electron microscopy of an edge view of the sample.

The samples were cooled to 1.8K by immersing them into liquid He in a specially constructed dewar from which He vapor was continually pumped. The photoluminescence was excited by focusing UV light from either a He-Cd laser (325 nm) or a tripled Nd:YAG laser (355 nm) onto the samples, which were either the quantum well structure or a 1.5μ -thick single crystal that was grown by methods described previously.⁹ The photoluminescence was focused onto the entrance slit of a 50-cm monochromator and dispersed onto an optical multichannel analyzer. The data were then transferred to a computer for storage and analysis.

III. Results and Discussion

We assume that the film was reasonably crystalline. All three materials, Si, CaF_2 and CuCl , have cubic crystal structures and nearly identical lattice constants (.543 nm, .546 nm, and .542 nm, respectively). Epitaxial films of both CaF_2 ⁸ and CuCl ¹⁰ on Si have been reported. We have examined x-ray diffraction patterns of quantum-well structures grown by the procedures described in the preceding section, and have not observed features that would indicate the presence of polycrystalline overlayers. However, the resolution of the diffractometer used was not sufficient to identify the diffraction peaks positively from thin epitaxial film of CaF_2 or CuCl against the background of diffraction peaks from the Si substrate. The only other evidence for the crystalline quality of the films was the fact that

the exciton emission in the photoluminescence spectra at low excitation density was remarkably intense, and no peaks were observed that could be attributed to impurities or defects.

In the quantum well structure, the CaF_2 serves essentially three purposes: (1) a structural template on which to grow crystalline CuCl , (2) an optically transparent confinement layer for holes and electrons, since the bandgap of CaF_2 (~ 10 eV) is so much larger than that of CuCl (~ 3.5 eV), and 3) a protective barrier that prevents reduction of the CuCl by the Si substrate and disproportionation of the CuCl induced by adsorption and in-diffusion of water. The role of chemically inert shield is extremely important.

We have performed experiments in which powdered CuCl and Si were sealed in quartz ampoules and heated to above 400°C . These samples turned a reddish color, and x-ray powder diffractometry indicated the presence of elemental Cu in the mixtures (see Fig.2). Thus, the intimate Si- CuCl interface is thermodynamically unstable with respect to the formation of silicon chlorides and Cu metal. Also, CuCl is extremely hygroscopic. Photoluminescence analysis of bulk CuCl crystals has shown large numbers of defect states that may be related to O^{--} impurities; in any case, a substantial amount of oxygen was observed by Auger depth profiling in CuCl crystals exposed to air.¹¹ We have also observed that thin films of CuCl exposed to atmosphere for extended times turn green, indicating the presence of Cu^{+2} species. Since we have not detected any interaction between powders of CuCl and CaF_2 heated to 300°C for days by x-ray diffractometry, we conclude that they are thermodynamically stable with respect to each

other. Therefore, a rather remarkable set of coincidences conspire to make $\text{CaF}_2/\text{CuCl}/\text{CaF}_2$ an ideal structure for studying the optical properties of CuCl quantum wells.

Photoluminescence spectra from a low density of excitons were excited using a He-Cd laser, which has a low average power. These spectra, collected for a sample temperature of 1.8K, are shown in Fig.3 for both the 150Å CuCl quantum well structure and for a 1.5μ-thick CuCl single crystal. The absolute intensity of the photoluminescence from the bound exciton of the thin film was roughly a factor of three less intense than that of the corresponding feature from the single crystal, even though the single crystal was two orders of magnitude thicker. In both cases, the bound exciton was the most intense feature in the spectra. The single-crystal spectrum contains several other peaks: the one at the lowest wavelength is the free exciton decay, and the remaining features have been assigned to impurity states.¹¹

On the other hand, the thin film spectrum contains only a small free exciton peak in addition to the bound exciton feature. A possible explanation for this observation is that the thin film has fewer impurities, since it is protected by a CaF_2 layer, whereas the single crystal has been exposed to the atmosphere and may contain water-related impurities. In any case, the rather high intensity and the clean appearance of the photoluminescence from the thin film support the assumption that the film has a reasonable crystalline quality. If the film did contain a high defect density, we would expect that non-radiative transitions would suppress the luminescence

from the quantum well and give rise to several additional peaks in the spectrum.

Photoluminescence spectra from a much higher density of excitons were excited using a tripled Nd:YAG laser, which delivers a very high average power in short (\sim nanosecond) pulses. In Fig.4, representative spectra are compared for both the quantum well and the single crystal. We also observe striking differences in these two spectra. The intensity ratio for the free-exciton to bound-exciton emissions is much larger in the quantum well than in the bulk sample. All the features in the quantum well spectrum are broader than their counterparts in the single-crystal spectrum, and the excitonic molecule peak in the quantum well is significantly blue-shifted with respect to the single-crystal excitonic molecule.

The CuCl film thickness should be too large for the differences observed between the two high exciton density spectra to be the result of quantum size effects, since the Bohr radius of the exciton is $\sim 6\text{\AA}$. Part of the difference observed for the shape of the spectra may be the result of a density-of-states effect. Since the thickness of the quantum well is small compared to the normal free-exciton mean free path, the exciton density of states should be two-dimensional (i.e., $dN(\epsilon)/d\epsilon = \pi/2$ for a dispersion relation $\epsilon = k^2/2$), rather than three-dimensional ($dN(\epsilon)/d\epsilon = \pi\epsilon^{1/2}$) as in the bulk crystal. However, the width of the free exciton and excitonic molecule features in the quantum well also indicate that the effective temperature of these excitons is much higher than that in the CuCl single crystal. This would be the case, for instance, if the lifetime of the excitons in

the quantum well were shorter than in the bulk crystal, which would mean that the excitons would decay before they could come into thermal equilibrium with the lattice. In this case, such a shortened radiative lifetime of the excitons could be the result of collisions with the walls of the quantum well or with other excitons.

IV. Summary

In conclusion, we have grown deep quantum wells consisting of CuCl sandwiched between protective layers of CaF_2 on Si(111) substrates. We have shown that exciton photoluminescence is easily observable for a single CuCl film as thin as 150Å, and that excitonic molecules can be excited in such a structure. The relatively intense luminescence and absence of defect states for low exciton densities is evidence for good crystalline quality of the quantum wells. At high exciton densities, the photoluminescence of the thin film was markedly different from the bulk CuCl, which demonstrated that a quantum well thickness of 150Å is sufficient to cause significant perturbation of the excitons. Thus, $\text{CaF}_2/\text{CuCl}/\text{CaF}_2$ quantum wells have a great deal of promise for the study of exciton spectroscopy and dynamics in two-dimensional systems.

V. Acknowledgments

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Figure Captions

- FIG. 1 - A schematic diagram of the deep-quantum-well structure studied in this investigation. The outer CaF_2 film transmitted both the incident laser excitation and the CuCl luminescence.
- FIG. 2 - The x-ray powder pattern of a Si/CuCl mixture heated in a closed quartz ampoule to 400°C . Strong diffraction peaks from elemental Cu are evident. The resolution of the diffractometer is not sufficient to resolve the Si and CuCl peaks.
- FIG. 3 - Photoluminescence spectra of (top) a 150\AA -thick CuCl film between two 150\AA CaF_2 layers and (bottom) a 1.5μ -thick CuCl single crystal. F.E. designates the free exciton and B.E. is the bound exciton. The excitation source was a He-Cd laser, and the sample temperature was 1.8K . These spectra are representative of low exciton density emission.
- FIG. 4 - Photoluminescence spectra of (top) a 150\AA -thick CuCl film between two 150\AA CaF_2 layers and (bottom) a 1.5μ -thick CuCl single crystal. E.M. is the excitonic molecule emission, and M_{\perp} and M_{\parallel} denote excitonic molecules associated with transverse and longitudinal final state excitons, respectively. The excitation source was a tripled Nd:YAG laser, and the sample temperature was 1.8K . These spectra are representative of high exciton density emission.

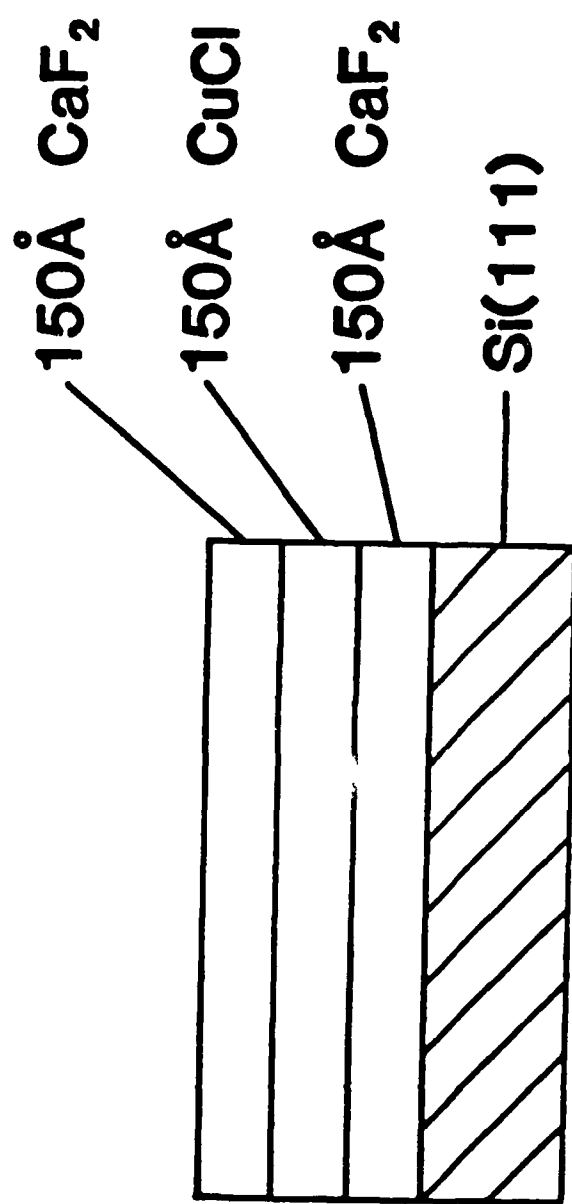


Fig. 1

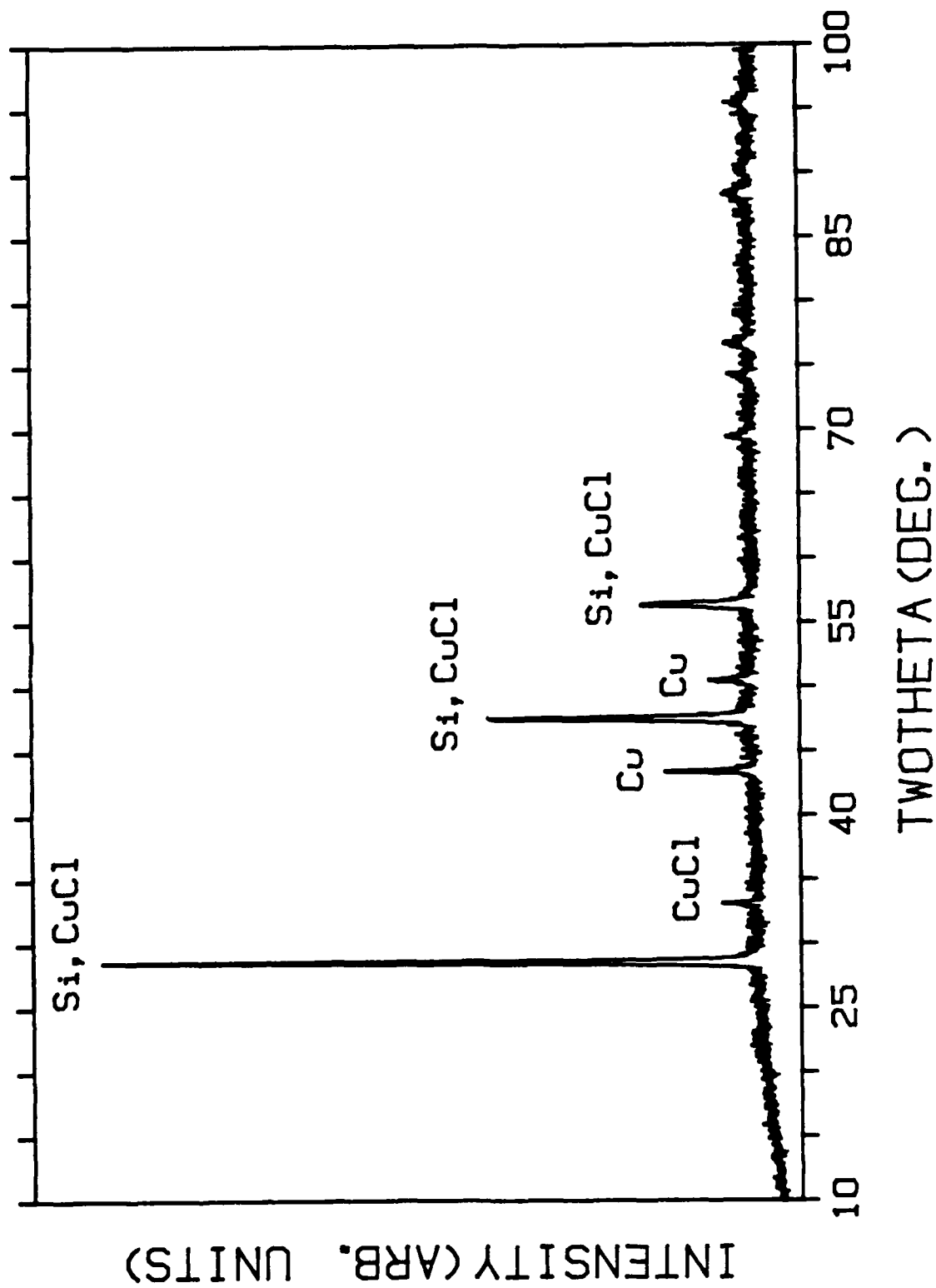


FIG. 2

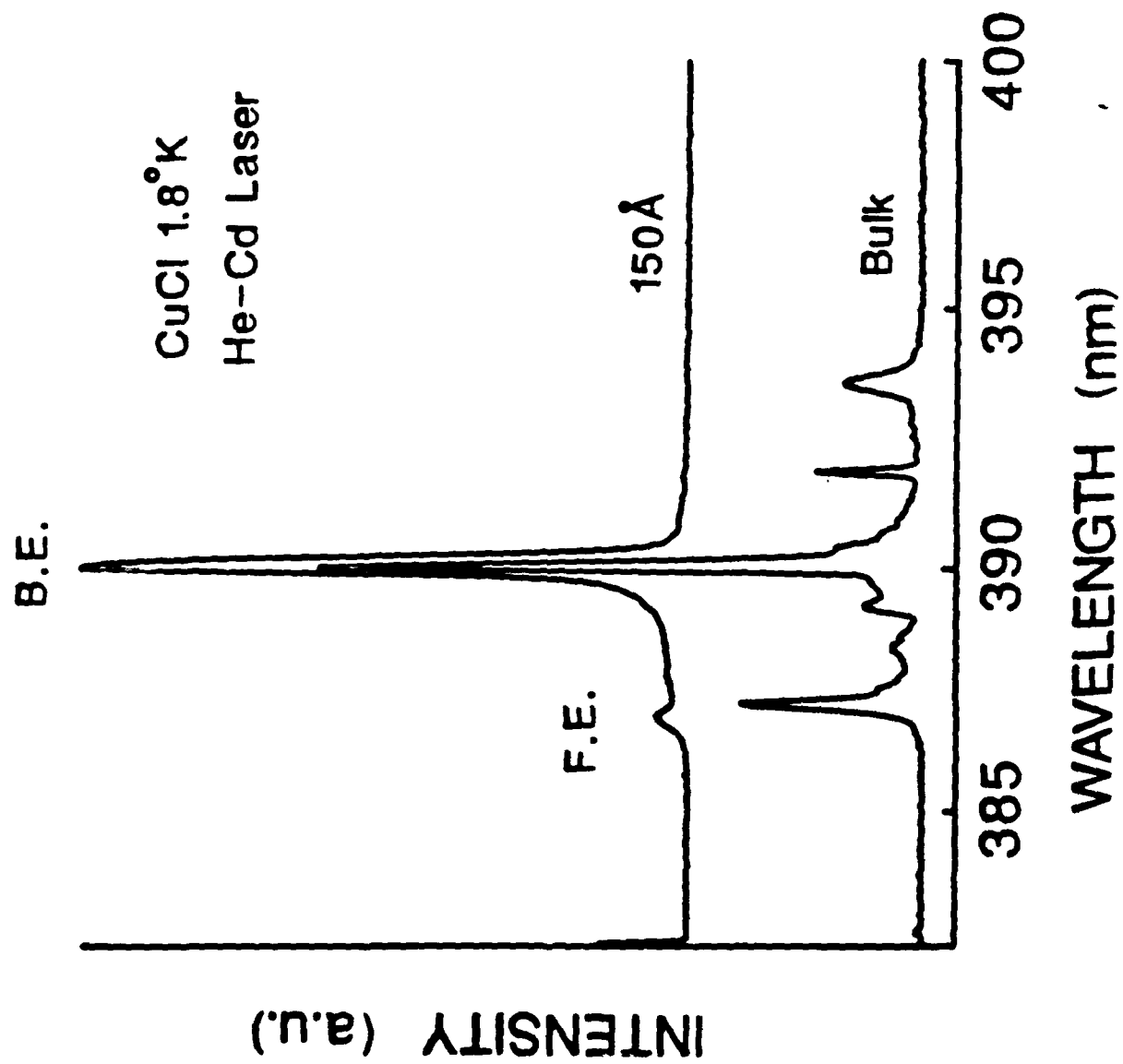


FIG. 3

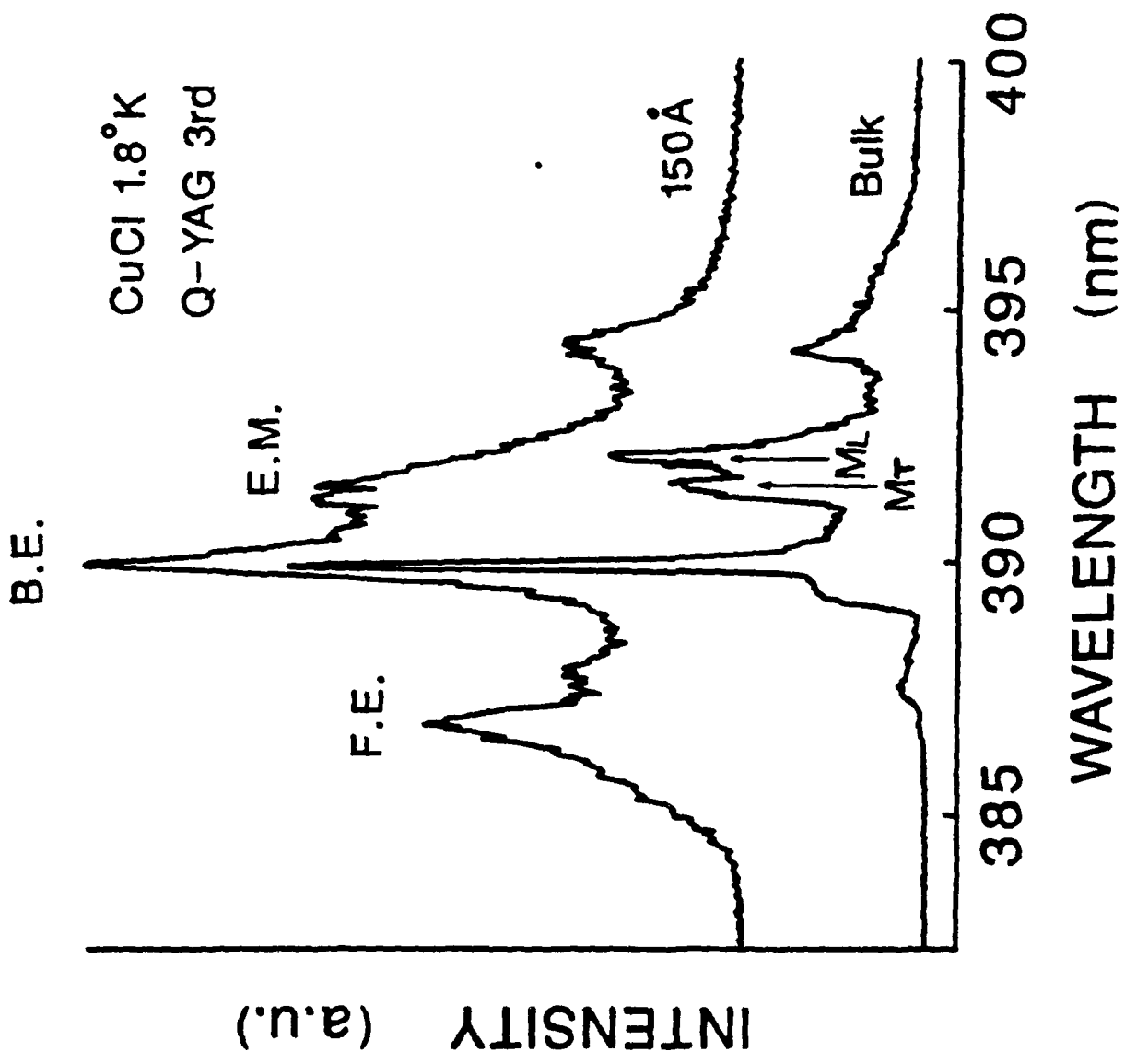


FIG 4

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